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(54) Title: LAUNDRY DETERGENT BARS CONTAINING FABRIC SOFTENING CLAY

(57) Abstract

A laundry bar containing from about 10 % to about 60 % by weight anionic surfactant, from about 5 % to about 60 % by weight detergent builder, about 1 % to about 30 % of a smectite-type softening clay, and a polymeric clay flocculating agent at a level of about 0.001 % to about 30 % by weight of the fabric softening clay. A preferred clay flocculating agent is a poly(ethylene oxide) having an average molecular weight of 100.000 to about 10 million. An optionally-added detergent chelant is preferably alkali metal, alkali earth metal, and heavy metal salts of diethylenetriamine penta (methylene phosphonic acid), diethylenetriamine penta (acetic acid), ethylenediamine tetra (methylene phosphonic acid), ethylenediamine tetra (acetic acid), and mixtures thereof.

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LAUNDRY DETERGENT BARS CONTAINING FABRIC SOFTENING CLAY

BACKGROUND OF THE INVENTION

The invention relates to improved laundry detergent bars. More particularly, it relates to laundry detergent bars comprising anionic detergent surfactant, a detergent builder, and fabric softening clay.

Detergent compositions in the form of synthetic detergent granules and liquids are used in many societies to launder clothes, particularly in those societies where mechanical washing machines are common. In portions of such societies, and more frequently in societies where mechanical washing machines are not common, laundry detergent bars comprising synthetic organic surfactants and detergency builders are used in the laundering of clothes.

Technical developments in the field of laundry detergent bars have concerned formulating bars which are effective in cleaning clothes; which have acceptable sudsing characteristics in warm and cool water and in hard and soft water; which have acceptable in-use wear rates, hardness, durability, and feel; which have low smear; and which have a pleasing odor and appearance. Examples of laundry bars include those described in the following Patents and publications: U.S. Patent 3,178,370 (issued to Okenfuss on April 13, 1965 and incorporated herein by reference) describes laundry detergent bars comprising sodium alkylbenzene sulfate (ABS), sodium tripolyphosphate, sodium bicarbonate, trisodium orthophosphate, and water, and processes for making these; Philippine Patent 13,778 (issued to Anderson on September 23, 1980) describes synthetic detergent laundry bars containing surfactant, alkali metal pyrophosphate, from about 18% to about 60% alkaline earth metal carbonate, and from about 1% to about 20% water; U.S. Pat. 4,543,204 (issued to Gervasio on September 24, 1985) discloses laundry detergent bars containing 10 to 35% of higher fatty alkyl sulfate, and from 1 to 10% of higher fatty acid which makes the bars more resistant to breaking on handling and storage; U.S. Patent 5,089,174, issued to Kaw et al, on Feb. 18, 1992, discloses an improved laundry bar comprising a mixture of anionic surfactants comprising

alkyl sulfate and alkylbenzene sulfonate, wherein fatty alcohol is added to advantageously reduce bar wear rate and improve solubility. Surfactant ratios of 90/10 to 10/90 by weight of alkyl sulfate/alkylbenzene sulfonate are disclosed; and Philippine Patent 26,860 (issued Nov. 16, 1982 to Unilever) discloses a laundry bar containing surfactant which is at least 1/3 primary alkyl sulfate and 12-60% builder consisting of at least two alkali metal phosphate selected form orthophosphate, pyrophosphate, and tripolyphosphate.

Methods for making laundry detergent bars are well known in the art. Examples of methods and processes for making laundry bars include those described in the following Patents and publications: Philippine Patent 23,689 (issued Sept. 27, 1989 to Unilever) discloses a process for making a bar containing 7-45% detergent surfactant, comprising the steps of neutralizing with alkaline material (such as carbonate) the acid precursor of the detergent surfactant, in the presence of a desiccant/adsorbent material, such as oleum, sulfuric acid, and anhydrous sulfate, followed by the addition of other ingredients, prior to formation into bars; and Philippine Patent 24,551 (issued Aug. 3, 1990 to Unilever) discloses a process for making a bar containing 7-45% detergent surfactant and 0-60% builder, comprising the steps of neutralizing with alkaline material (such as carbonate) the acid precursor of the detergent surfactant, in the presence of 0.25 - 50% by weight of silica-containing material, such as crystalline aluminosilicate, silica gels, and amorphous silica, followed by the addition of other ingredients, prior to formation into bars.

Improvements in laundry bars have been made to improve the physical properties of bars by the use of clays. Examples of laundry bars comprising clays for use as a filler material include those described in the following Patents and publications: Philippine Patent 17712 (issued Nov. 19, 1984 to Unilever) discloses a bar containing detergent surfactant, builder and 0.5 - 45% of a sheet aluminosilicate filler, such as bentonite, and from 2.5 - 57% of a particulate substantially water-insoluble non-sheet-aluminosilicate filler, where the two fillers are 10-60% of the total bar by weight; Philippine Patent 18,128 (issued March 22, 1985 to Unilever) discloses a bar containing detergent surfactant, builder, 0.5 - 45% of a sheet aluminosilicate filler, and 10-60% of a non-builder, essentially water-soluble filler, where the two fillers are 10.5 - 60.5% of the bar by weight; and Philippine Patent 27,321 (issued June 8, 1993 to Colgate Palmolive) discloses a bar composition containing anionic surfactant, at least 15-70% of which is alkyl sulfate or alpha sulfo fatty alkyl methyl

ester, 3-10% zeolite as a principle builder, and up to 60% of a filler consisting of 4-9% netonite and the balance from calcium carbonate, sodium carbonate, sulfate, and mixtures thereof.

Laundry bars containing softening clays to improve the softening performance on clothes washed with such bars by the use of clays. Examples of laundry bars comprising softening clays include those described in the following Patents and publications: Philippine Patent 22,589 (issued Oct. 17, 1988 to Firmenich & Cie) discloses a laundry bar containing anionic surfactant, builder, and from 5-50% of a softening agent, which can include up to 40% of a smectite clay, such as bentonite, having an ionic exchange capacity of higher than 50 meq/100gm.

However, none of the bars described as containing clay are completely satisfactory in performance. Therefore, there remains a need to improve the fabric softening clothes washed using laundry bars while maintaining good soil cleaning and removal, and other physical bar properties.

In areas where granular detergent compositions are used, particulate softening clays are often employed, alone or in combination with other softening ingredients, as a portion of the granular detergent composition itself, or as a separate laundry additive added to the water used to rinse the clothes. It is known that clay flocculating agents can be used with such particulate softening clays in granular detergent compositions to improve the deposition of such clays, and hence their clothes softening performance. Examples of granular detergent compositions containing softening clays and clay flocculating agents include those described in the following Patents and publications: European Patent Publication EP 0,299,575-A1, published Jan. 18, 1989 (The Procter & Gamble Company) discloses detergent compositions containing a fabric softening smectite-type clay and a polymeric clay flocculating agent; and European Patent Publication EP 0,313,146-A1, published Apr. 26, 1989 (The Procter & Gamble Company) discloses detergent compositions containing a fabric softening smectite-type clay treated with an organic humectant to enhance its softening benefit, and optionally containing a polymeric clay flocculating agent.

An object of the present invention is to improve the clothes softening performance of laundry bars containing softening clay, while providing good surfactant mileage, cleaning, wear rate, solubility, and other bar aesthetics.

SUMMARY OF THE INVENTION

The laundry detergent bars of the present invention comprise detergent surfactant, detergency builder, a fabric softening clay, and an effective amount of a clay flocculating agent to improve the clothes softening performance of the clay. Preferably, the bars comprise from about 10% to about 60% by weight anionic surfactant, from about 5% to about 60% by weight detergent builder, from about 1% to about 30% of a smectite-type softening clay, and a polymeric clay flocculating agent at a level of about 0.001% to about 30% by weight of the softening clay.

Preferably, the polymeric clay flocculating agent is selected from the group consisting of poly(ethylene oxide), poly(acrylic amide), and poly(acrylate) having a molecular weight of about 100,000 to about 10 million.

DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims distinctly pointing out and particularly claiming that which is regarded as the invention, it is believed that the invention can be better understood through a careful reading of the following detailed description of the invention. In this specification all percentages are by weight, all temperatures are expressed in degrees Celsius, molecular weights are in weight average, and the decimal is represented by the point(.), unless otherwise indicated.

Detergent surfactant

Laundry bars of the present invention typically comprise 10% to about 60% of an anionic surfactant. A preferred anionic surfactant for use is an alkyl sulfate (AS) having an alkyl chain of from 10 to 20 carbon atoms, a branched-chain alkylbenzene sulfonate (ABS) having an alkyl chain of from 10 to 22 carbon atoms, a linear-chain alkylbenzene sulfonate (LAS) having an alkyl chain of from 10 to 22 carbon atoms, and mixtures thereof. Preferred bars comprise about 15% to about 40%, more preferably from about 18% to about 32%, such anionic surfactant.

The alkyl portion of said ABS or LAS surfactant preferably contains from 10 to 16 carbon atoms, more preferably from 10 to 14 carbon atoms. Most preferably, the alkylbenzene sulfonate surfactant is LAS.

The alkyl portion of the AS surfactant preferably contains from 10 to 18 carbon atoms, more preferably from 12 to 16 carbon atoms. The AS surfactant can comprise a mixture of a longer-chain AS, such as one having 16 to 18 carbons, and a shorter-chain alkyl such as one having 11-13 carbons. Preferred AS surfactants include coconut alkyl sulfate, tallow alkylsulfate, and mixtures thereof; most preferably, coconut alkyl sulfate.

The cation for the ABS, LAS and the AS is preferably sodium, although other useful cations include triethanolamine, potassium, ammonium, magnesium, and calcium, or mixtures thereof.

A preferred anionic surfactant comprised a mixture of AS and alkylbenzene sulfonate. A mixture of AS and alkylbenzene sulfonate surfactant typically comprises a ratio by weight of AS surfactant: alkylbenzene sulfonate from 10:90 to 95:5, more preferably from 40:60 to 95:5, and most preferably from 75:25 to about 90:10. In a preferred embodiment, the laundry bar comprises an anionic surfactant comprising a molar ratio mixture of AS and LAS of from 80:20 to about 90:10, more preferably from about 82:18 to about 88:12, and most preferably from about 84:16 to about 87:13. Such detergent bars are disclosed in co-pending Philippines Patent application 47165-A, filed Oct. 29, 1993, by Rodney M. Wise and Belal U. Siddique, assigned to The Procter & Gamble Company.

Detergent Builder

The laundry bars of the present invention comprise from about 5% to about 60% by weight detergent builder. Preferred laundry bars comprise from about 5% to about 30% builder, more preferably from about 7% to about 20%, by weight of the bar. These detergent builders can be, for example, water-soluble alkali-metal salts of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof. A preferred builder is a water-soluble alkali-metal salt of tripolyphosphate, and a mixture of tripolyphosphate and pyrophosphate. The builder can also be a non-phosphate detergent builder. Specific examples of a non-phosphorous, inorganic detergency builder include water-soluble inorganic carbonate and bicarbonate salts. The alkali metal (e.g., sodium and potassium) carbonates, bicarbonates, and silicates are particularly useful herein.

Sodium carbonate is a particularly preferred ingredient in laundry bars, since in addition to its use as a builder, it can also provide alkalinity to the laundry bar for improved detergency, and also can serve as a neutralizing agent for acidic components added in the bar processing. Sodium carbonate is particularly preferred as a neutralizing inorganic salt for an acid precursor of an anionic surfactant used in such laundry bars such as the alkyl sulfuric acid and alkyl benzene sulfonic acid.

Also useful are aluminosilicate ion exchange materials. These aluminosilicates can be crystalline or amorphous in structure and can be either naturally occurring or synthetically derived. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula:

$$Na_{12}[(AlO_2)_{12}.(SiO_2)_{12}].xH_2O$$

wherein x is from about 20 to about 30, especially about 27.

Water-soluble organic detergency builders, for example alkali metal, ammonium and substituted ammonium polycarboxylates, are also useful herein. Specific examples of useful polycarboxylate builder salts include sodium, potassium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acid, polyacrylic acid, polymaleic acid, acrylic acid-maleic acid copolymers, polyaspartic acid, and citric acid, or such acids per se. These polymers typically have an average molecular weight of less than about 100,000, more preferably about 1000-10,000. Other useful polycarboxylate detergency builders are the materials set forth in U.S. Pat. 3,308,067 issued to Diehl on March 7, 1967, incorporated herein by reference. Mixtures of detergent builders can be used in the present invention.

Co-polymers of acrylic acid and maleic acid are preferred as auxiliary builders, since it has been observed that their use in combination with the fabric softening clay and the clay flocculating agent further stabilizes and improves the clay deposition and fabric softening performance.

Specific preferred examples of builders include sodium tripolyphosphates (STPP) and sodium pyrophosphates (TSPP), and mixtures thereof. Other specifically preferred examples of builders include zeolite and polycarboxylates.

Fabric Softening Clay

The fabric softening clay is preferably a smectite-type clay. The smectite-type clays can be described as expandable, three-layer clays; i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least about 50 meq/100 g. of clay. Preferably the clay particles are of a size that they can not be perceived tactilely, so as not to have a gritty feel on the treated fabric of the clothes.

There are two distinct classes of smectite-type clays; in the first, aluminum oxide is present in the silicate crystal lattice; in the second, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectite are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)_2(OH)_2$, for the aluminum and magnesium oxide type clay, respectively. It is to be recognized that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectite, while metal cations such as Na+, Ca++, as well as H+, can be co-present in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

The three-layer, alumino-silicates useful herein are further characterized by a dioctahedral crystal lattice, while the three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted hereinabove, the clays employed in the compositions of the instant invention contain cationic counterions, such as protons, sodium ions, potassium ions, calcium ions, magnesium ions, and the like. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a Smectite-type clay is expressed by the following equation:

$$\text{Smectite-type clay (Na)} + NH_4OH = \text{Smectite-type clay } (NH_4) + NaOH$$

Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation

exchange capacity (sometimes termed "base exchange capacity") in terms of milli-equivalents per 100g of clay (meq/100g).

Cation exchange capacity of the clay is a well-known parameter in determining the clay's effectiveness as a fabric softener. The cation exchange capacity may be determined by well-established analytical techniques. See, for example, H van Olphen, "Clay Colloid Chemistry", Interscience Publishers, 1963, and the relevant references cited therein. It is preferred that the clay particles used in the present invention have a cation exchange capacity of at least about 50 meq/100g.

The smectite-type clays used in the compositions herein are well-known and many are commercially available. Such clays include, for example, montmorillonite, volchouskoite, nontronite, bentonite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under various trade names, for example, Thixogel No. 1 (also, "Thixo-Jell") and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay No. 325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R. T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained mixtures of the various discreet metal entities. Such mixtures of the smectite minerals are suitable for use herein.

While any of the smectite-type clays described herein are useful in the present invention, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite-type clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in the instant compositions from the standpoint of product performance. On the other hand, certain smectite-type clays are sufficiently contaminated by other silicate minerals that their ion exchange capacities fall below the requisite range; such clays are of no use in the instant compositions.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14A x-ray diffraction pattern. This characteristic pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type

minerals for use in the composition disclosed herein.

Acid-treated bentonite or other softening clay, such as those disclosed in Philippine Patent No. 18,297, issued May 20, 1985, assigned to Unilever, can also be used as the fabric softening clay.

The fabric softening clay can be added to the bar to provide about 1% to about 30% by weight of the bar, more preferably from about 5% to about 20%, and most preferably about 8% to 14%.

Clay Flocculating Agent

The polymeric clay flocculating agent is selected to provide improved deposition of the fabric softening clay. Typically such materials have a high molecular weight, greater than about 100,000. Examples of such materials can include long chain polymers and copolymers derived from monomers such as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Gums, like guar gums, are suitable as well.

A preferably clay flocculating agent is selected from high molecular weight polyethylene oxide, polyacrylic amide, and polyacrylate having a molecular weight of about 100,000 to about 10 million. It has been found that the use of a clay flocculating agent in a laundry bar containing softening clay provides surprisingly improved softening clay deposition onto the clothes and clothes softening performance, compared to that of laundry bars comprising softening clay alone. The amount of clay flocculating agent to be used in the laundry bar is preferably an effective amount to provided noticeably improved fabric softening performance. The amount of clay flocculating agent to be used can vary depending on the type of clay flocculating agent employed, the type of fabric softening clay, and the types and levels of other detergent adjuvants in the laundry bar. The level of clay flocculating agent is conveniently referred to in terms of its weight percentage of the amount of fabric softening clay in the bar. The bar will typically comprise, by weight of fabric softening clay, about 0.001% to about 30% clay flocculating agent, more preferably about 0.01% to about 15%, and most preferably about 0.5% to about 5%.

The effectiveness of the clay flocculating agent in general becomes greater as the molecular weight of the flocculating agent increases. The polymers typically have

an average molecular weight of about 100,000 to about 10 million, more preferably from about 150,000 to about 5 million. As with the level of clay flocculating agent, selection of an appropriate polymer molecular weight will depend on the type of clay and the type of flocculating agent, as well as the other components of the composition.

The preferred clay flocculating agent is a poly(ethylene oxide) polymer.

OPTIONAL COMPONENTS

The detergent bars of the present invention can contain up to about 70% by weight of optional ingredients commonly used in detergent products. A typical listing of the classes and species optional surfactants, optional builders and other ingredients useful herein appears in U.S. Pat. No. 3,664,961, issued to Norris on May 23, 1972, and EP 550,652, published on April 16, 1992, incorporated herein by reference. The following are representative of such materials, but are not intended to be limiting.

Optional Detergent Surfactant: Optional detergent surfactants can be included at a level up to about 10%, more preferably from about 0.1% to about 5%, by weight of the composition. The types of detergent surfactants that can be used as optional surfactants include anionic, cationic, nonionic, amphoteric and zwitterionic surfactant, and mixtures thereof.

Optional anionic surfactants useful herein as auxiliary surfactants include:

Sodium alkyl glyceryl ether sulfates, especially those ethers of higher alcohols derived from tallow and coconut oil;

Sodium coconut oil fatty acid monoglyceride sulfonates and sulfates;

Sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates, and sodium or potassium salts of methyl ester R-CH(SO_3M)-COOR', wherein R is C_8-C_{22} alkyl or alkenyl, R' is C_1-C_4 alkyl, and M is a counter ion, preferably Na or K, such as disclosed in WO-93-05013, published March 18, 1992; sulfonates;

Secondary alkyl sulfates having an alkyl chain of from 10 to 20 carbon atoms;

Higher fatty acids (i.e., "soaps") such as the sodium, potassium, ammonium and alkanolammonium salts of higher fatty acids. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap;

Alkylalkoxy sulfate comprising an alkyl portion of from 6 to 18 carbon atoms and an alkoxy portion comprising, an average, from about 0.5 to about 20 moles of alkoxy, preferably ethoxy, units, more preferably from about 0.5 to about 5 ethoxy units; and

Alkyl ethoxy carboxylates of the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$, wherein R is a C_6 to C_{18} alkyl; x ranges from 0 to 10, and the ethoxylate distribution is such that on a weight basis, the amount of material where x is 0 is less than 20%, the amount of material where x is greater than 7 is less than 25%, and wherein the average x is 2-4 when the average R is C_{13} or less, and is 3-6 when R is greater than C_{13}; and M is an alkali metal, alkali earth metal, ammonium, mono-, di-, and tri-ethanol ammonium.

Other optional surfactants can be nonionic, and can include:

Alkyl polysaccharides, alkyl polyglucosides, such as described in U.S. Patent 4,565,647, Llenado;

Polyhydroxy fatty acid amides, of the formula R-C(O)-N(R')-Z, wherein R is C_5-C_{31} hydrocarbyl, preferably C_{11}-C_{17} alkyl or alkenyl, R' is H, C_1-C_4 hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably methyl, and Z is polyhydroxy(linear)hydrocarbyl chain having at least 3 hydroxyls directly connected to the chain, preferably $-CH_2-(CHOH)_4-CH_2OH$, such as described in EP 550,652;

Semi-polar nonionic surfactants, such as water-soluble amine oxides, water-soluble phosphine oxide surfactants, and water-soluble sulfoxide surfactants; and

Water-soluble nonionic synthetic surfactants broadly defined as compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature)

with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Optional surfactants also include ampholytic surfactants which include aliphatic derivatives of heterocyclic secondary and tertiary amines; zwitterionic surfactants which include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds; water-soluble salts of esters of alpha-sulfonated fatty acids; alkyl ether sulfates; water-soluble salts of olefin sulfonates; beta-alkyloxy alkane sulfonates; betaines having the formula $R(R^1)_2N^+R^2COO^-$, wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group or C_{10}-C_{16} acylamido alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl and R_2 is a C_1-C_5 hydrocarbyl group, preferably a C_1-C_3 alkylene group, more preferably a C_1-C_2 alkylene group. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C_{12-14} acylamidopropylbetaine; C_{8-14} acylamidohexyldiethyl betaine; 4[C_{14-16} acylmethylamidodiethylammonio]-1-carboxybutane; C_{16-18} acylamidodimethylbetaine; C_{12-16} acylamidopentanediethylbetaine; and [C_{12-16} acylmethylamidodimethylbetaine. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines; and the sultaines having the formula $(R(R^1)_2N^+R^2SO_3^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group, more preferably a C_{12}-C_{13} alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl, and R^2 is a C_1-C_6 hydrocarbyl goup, preferably a C_1-C_3 alkylene or, preferably, hydroxyalkylene group. Examples of suitable sultaines include C_{12}-C_{14} dimethylammonio-2-hydroxypropyl sulfonate, C_{12}-C_{14} amido propyl ammonio-2-hydroxypropyl sultaine, C_{12}-C_{14} dihydroxyethylammonio propane sulfonate, and C_{16-18} dimethylammonio hexane sulfonate, with C_{12-14} amido propyl ammonio-2-hydroxypropyl sultaine being preferred.

In addition to the auxiliary surfactants mentioned above, a hydrotrope, or mixture of hydrotropes, can be present in the laundry detergent bar. Preferred hydrotropes include the alkali metal, preferably sodium, salts of tolune sulfonate, xylene sulfonate, cumene sulfonate, sulfosuccinate, and mixtures thereof. Preferably, the hydrotrope, in either the acid form or the salt form, and being substantially anhydrous, is added to the linear alkyl benzene sulfonic acid prior to its neutralization. The hydrotrope will preferably be present at from about 0.5% to about 5% of the laundry detergent bar.

Detergent Chelant: A particularly preferred optional component of the present invention is a detergent chelant. Such chelants are able to sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali metal earth cations (such as magnesium and calcium), and most preferably, heavy metal cations such as iron, manganese, zinc and aluminum. Preferred cations include sodium, magnesium, zinc, and mixtures thereof. The detergent chelant is particularly beneficial for maintaining good cleaning performance and improved surfactant mileage, despite the presence of the softening clay and the clay flocculating agent. Without being bound by any theory, it is believed that the softening clay structure contains iron (Fe) and other transition metal ions. In the washing process, substitution by calcium and magnesium in the wash water and in the soils of the iron or other transition metal ions can occur, dislodging the transition metal ion into the wash solution. These metal ions are known to contribute to yellowing and graying of fabrics. The detergent chelant can reduce significantly these effects.

The detergent chelant is preferably a phosphonate chelant, particular one selected from the group consisting of diethylenetriamine penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelant, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) diethylenetriamine penta (acetate), and mixtures thereof.

Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least 1:1, preferably at least 2:1.

The detergent chelant can be included in the laundry bar at a level up to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 2%, most preferably from about 0.5% to about 1.0%. Such detergent chelant component can be used beneficially to improve the surfactant mileage of the present laundry bar, meaning that for a given level of anionic surfactant and level of detergent chelant, equivalent sudsing and cleaning performance can be achieved compared to a similar bar containing a higher level of the anionic surfactant but without the detergent chelant.

The detergent chelants can be used in a particulate or granular form, or in an aqueous or solvent solution. Methods of preparing such salts and complexes are well known, and are described in U.S. Patent 4,259,200, issued 3/31/81, the disclosure of which is incorporated by reference. A preferred form is a particulate or a granular form. Such particulate or granules of the detergent chelant can be formed with an organic or inorganic binding material. A suitable organic binding material is e.g. a nonionic surfactant. Suitable inorganic binding materials include sodium tripolyphosphate, sodium carbonate, magnesium sulfate, and the like. Any granulation technique known in the art can be employed, e.g. by spraying a molten nonionic surfactant on to a moving bed of the dried metal complex, fluid-bed drying, etc.

Enzyme: Another particularly preferred component is a detergent enzyme. Non-limiting types of enzymes include cellulase, lipase, amylase, lipolase, malease, protease, catalase, maltase, and phosphatase. Particularly preferred are cellulase, lipase, protease, amylase, and mixtures thereof. Enzymes are advantageously used at levels up to 5%. A particularly cellulase enzyme which provides fabric care and softening benefits by in situ enzymatic hydrolysis of amorphous, non-crystalline cellulose, which is associated with damaged cellulosic fibers. A particularly preferred cellulase is Carezyme® cellulase, supplied by Novo Nordisk.

Another useful optional component of the laundry detergent bars of this invention is silicate, especially sodium or magnesium silicate. Sodium silicate can be used at up to about 15% silicate solids having a weight ratio of SiO_2 to Na_2O between about 1.0:1 and about 3.4:1.

Another preferred additional component is a layered, crystalline alkaline silicate. A preferred commercially-available layered silicate is known as "SKS-6" ($Na_2Si_2O_5$),

is available from Hoechst, and is disclosed in U.S. Patent 4,664,839, issued May 12, 1987. Another preferred layered silicate is disclosed in EP Publication 550,048, July 7, 1993 (Kao), which discloses a synthesized crystalline material having a chain structure and having a composition represented by the following formula in anhydrous form:

$$xM_2O \cdot ySiO_2 \cdot zM'O,$$

wherein M represents Na and/or K; M' represents Ca and/or Mg; y/x is 0.5 to 2.0; and z/x is 0.005 to 1.0, said chain structure appearing as a main scattering peak in Raman spectra at least 970 ± 20 cm^{-1} in the range of 900 to 1200 cm^{-1}. Such layered silicate material is particularly preferred because it can provide both alkalinity, and calcium sequestering or builder functionality.

Another preferred additional component of the laundry bar is fatty alcohol having an alkyl chain of 8 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms. Fatty alcohol is effective at reducing the bar wear rate and smear (mushiness) of the present laundry bars. A preferred fatty alcohol has an alkyl chain predominantly containing from 16 to 18 carbon atoms, so-called "high-cut fatty alcohol," which can exhibit less base odor of fatty alcohol relative to broad cut fatty alcohols. Typically fatty alcohol is contained in the laundry bar at up to a level of 10%, more preferably from about 0.75% to about 6%, most preferably from about 2% to about 5%. The fatty alcohol is generally added to the formulation of the present invention as free fatty alcohol. However, low levels of fatty alcohol can be introduced into the bars as impurities or as unreacted starting material. For example, laundry bars based on coconut fatty alkyl sulfate can contain, as unreacted starting material, from 0.1% to 3.5%, more typically from 2% to 3%, by weight of free coconut fatty alcohol on a coconut fatty alkyl sulfate basis.

The free fatty alcohol can also serve as a suds booster, for reinforcing and extending suds generation and longevity. For suds boosting, a preferred fatty alcohol has an alkyl chain predominantly having 12 to 14 carbon atoms, used in the composition at a level from about 0.5% to 3%. Preferably, a narrow-cut C_{12} alkyl alcohol is used at a level of 0.5% to 2%.

Another preferred component of the laundry can include a soil release polymer. Such soil release polymers can be used at levels up to 5%, preferably at from about 0.05% to about 3%, more preferably from about 0.2% to about 1.0%. A soil release polymer can improve the multi-cycle cleaning of clothes washed with the laundry

bar. Preferred soil release polymer materials includes those disclosed in U.S. Patent 4,877,896, issued Oct. 31, 1989, and U.S. Patent 5,182,043, issued Jan. 26, 1993, herein disclosed by reference.

A preferred soil release polymer is a substantially linear, sulfoaroyl end-capped ester having a molecular weight of from about 500 to about 20,000, wherein said ester comprises, on a molar basis,

(i) from about 1 to about 2 moles of sulfobenzoyl end-capping units of the formula $(MO_3S)(C_6H_4)$-C(O)-, wherein M is a salt-forming cation;

(ii) from about 2 to about 50 moles of oxy-1,2-propyleneoxy units or mixtures thereof with oxyethyleneoxy units provided that the oxy-1,2-propyleneoxy:oxyethyleneoxy mole ratio is in the range from about 1:10 to about 1:1; and

(iii) from about 1 to about 40 moles of terephthaloyl units provided that the mole ratio of said units identified by (ii) and (iii) is from about 2:1 to about 1:24; and which further optionally comprises, per mole of said ester,

(iv) from 0 to about 30 moles of 5-sulfoisophthaloyl units of the formula $-(O)C(C_6H_3)(SO_3M)C(O)-$ wherein M is a salt-forming cation; or

(v) from 0 to about 25 moles of poly(oxyethylene)oxy units of the formula $-(OCH_2CH_2)_nO-$ wherein the average degree of ethoxylation n ranges from 2 to about 100; or

(vi) from 0 to about 30 moles of a mixture of said units (iv) and (v) at a (iv):(v) mole ratio of from about 29:1 to about 1:29.

Preferably, said substantially linear, sulfoaroyl end-capped ester comprises, on a molar basis,

(i) about 2 moles of sulfobenzoyl end-capping units of the formula $(MO_3S)(C_6H_4)$-C(O)-, wherein M is sodium;

(ii) about 14 moles of oxy-1,2-propyleneoxy units or mixtures thereof with oxyethyleneoxy units having a oxy-1,2-propyleneoxy:oxyethyleneoxy mole ratio in the range from about 1:0 to about 1:7; and

(iii) about 11 moles of terephthaloyl units; and

(iv) about 2 moles of 5-sulfoisophthaloyl units of the formula $-(O)C(C_6H_3)(SO_3M)C(O)-$ wherein M is sodium,

and wherein at least 20% of the ester has a molecular weight of from about 800-20,000.

Another preferred soil release polymer is a sulfonated poly-ethoxy/propoxy end-capped ester oligomer polymer, which comprises: (i) from about 1 to about 2 moles of sulfonated poly-ethoxy/propoxy end-capped units of the formula $((MO_3S)CH_2)_m(CH_2)_m(CH_2CH_2O)(RO)_n$-, wherein M is a salt forming cation selected from the group consisting of sodium and tetraalkylammonium, m is 0 or 1, R is ethylene, propylene or a mixture thereof, and n is from 0 to 2; (ii) from about 0.5 to about 66 moles of units selected from the group consisting of: a) oxyethyleneoxy units; b) a mixture of oxyethyleneoxy and oxy-1,2-propyleneoxy units wherein said oxyethyleneoxy units are present in an oxyethyleneoxy to oxy-1,2-propyleneoxy mole ratio ranging from 0.5:1 to about 10:1; and c) a mixture of a) or b) with poly(oxyethylene)oxy units wherein said poly(oxyethylene)oxy units have a degree of polymerization of from 2 to 4; provided that when said poly(oxyethylene)oxy units have a degree of polymerization of 2, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.33:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 3, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.22:1; and when said poly(oxyehtylene)oxy units have a degree of polymerization of 4, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.14:1; (iii) from about 1.5 to about 40 moles of terephthaloyl units; and (iv) from 0 to about 26 moles of 5-sulfoisophthaloyl units of the formula $-(O)C(C_6H_3)(SO_3M)C(O)-$ wherein M is a salt forming cation. Preferably, such ester oligomers has a molecular weight from about 500 to about 20,000, more preferably about 500 to about 5,000.

A specifically preferred ester oligomer polymer has the formula:

$$NaO_3S(CH_2CH_2O)_2\text{-}C(O)\text{-}(C_6H_4)\text{-}C(O)O\text{-}[\text{-}CH_2CRH\text{-}O\text{-}C(O)\text{-}(C_6H_4)\text{-}C(O)O\text{-}]_4\text{-}$$
$$\text{-}[\text{-}CH_2CRH\text{-}O\text{-}C(O)\text{-}(C_6H_4)SO_3Na\text{-}C(O)O\text{-}]_1\text{-}CH_2CH_2OCH_2CH_2SO_3Na$$

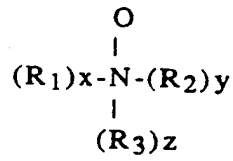
wherein R is H or CH_3 in a ratio of about 1.8:1.

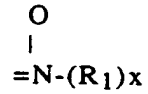
The soil release polymer can be added to the bar composition during the making process in a liquid or a granular form. In a preferred embodiment, the soil release polymer is in a low density, porous particulate form. Such porous soil release polymer form can be made by spray-drying a solution of the soil release polymer in liquid form, alone or with one or more carrier materials, to remove substantially all free water or other solvent liquid, by spray drying methods well known in the art.

Another preferred optional component in the laundry bar is a dye transfer inhibiting (DTI) ingredient to prevent diminishing of color fidelity and intensity in fabrics. A preferred DTI ingredient can include polymeric DTI materials capable of binding fugitives dyes to prevent them from depositing on the fabrics, and decolorization DTI materials capable of decolorizing the fugitives dye by oxidation. An example of a decolorization DTI is hydrogen peroxide or a source of hydrogen peroxide, such as percarbonate or perborate. Non-limiting examples of polymeric DTI materials include polyvinylpyrridine N-oxide, polyvinylpyrrolidone (PVP), PVP-polyvinylimidazole copolymer, and mixtures thereof.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R\text{-}A_x\text{-}P$; wherein P is a polymerizable unit to which an N-O goup can be attached or the N-O goup can form part of the polymerizable unit of the N-O group can be attached to both units: A is one of the following structures; -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic group or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:

I 

II 

wherein R_1, R_2, R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of a suitable polymeric backbone is polyvinyl, polyalkylene, polyester, polyether, polyamide, polyimide, polyacrylate and mixtures thereof. The polymer can include random or block copolymers where one monomer type is an amine N-oxide and the other

monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as "PVPI") are also preferred for use herein. Preferably the PVPI has an average molecular weight from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions can also contain a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. Examples of PVP are disclosed in, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the weight ratio of PEG to PVP is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

One or more of the polymeric DTI materials can also be combined with one or more of the decolorization DTI materials. The DTI material is advantageously used at levels in the bar up to about 10%, preferably from about 0.05% to 5%, more preferably from about 0.2% to about 2%.

Another preferred optional component in the laundry bar is a secondary fabric softener component in addition to the softening clay. Such materials can be used at levels of about 0.1% to 5%, more preferably from 0.3% to 3%, and can include:

amines of the formula $R_4R_5R_6N$, wherein R_4 is C_5 to C_{22} hydrocarbyl, R_5 and R_6 are independently C_1 to C_{10} hydrocarbyl. One preferred amine is ditallowmethyl amine; complexes of such amines with fatty acid of the formula R_7COOH, wherein R_7 is C_9 to C_{22} hydrocarbyl, as disclosed in EP No. 0,133,804; complexes of such amines with phosphate esters of the formula $R_8O\text{-}P(O)(OH)\text{-}OR_9$ and $HO\text{-}P(O)(OH)\text{-}OR_9$, wherein R_8 and R_9 are independently C_1 to C_{20} alkyl of alkyl ethoxylate of the formula -alkyl-(OCH_2CH_2); cyclic amines such as imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline, where higher alkyl is from 12 to 22 carbons and lower alkyl is from 1 to 4 carbons, such as described in UK Patent Application GB 2,173,827; and quaternary ammonium compounds of the formula $R_{10}R_{11}R_{12}R_{13}N^+X^-$, wherein R_{10} is alkyl having 8 to 20 carbons, R_{11} is alkyl having 1 to 10 carbons, R_{12} and R_{13} are alkyl having 1 to 4 carbons, preferably methyl, and X is an anion, preferably Cl^- or Br^-, such as $C_{12\text{-}13}$ alkyl trimethyl ammonium chloride.

Yet another optional component in the laundry bar is a bleach component. The bleaching component can be a source of ^-OOH group, such as sodium perborate monohydrate, sodium perborate tetrahydrate and sodium percarbonate. Sodium percarbonate ($2Na_2CO_3{\cdot}3H_2O_2$) is preferred since it has a dual function of both a source of HOOH and a source of sodium carbonate.

Another optional bleaching component is a peracid per se, such as a formula:

$$CH_3(CH_2)_w\text{-}NH\text{-}C(O)\text{-}(CH_2)_zCO_3H$$

wherein z is from 2 to 4 and w is from 4 to 10. (The compound of the latter formula where z is 4 and w is 8 is hereinafter referred to as NAPAA.) The bleaching component can contain, as a bleaching component stabilizer, a chelating agent of polyaminocarboxylic acids, polyaminocarboxylates such as ethylenediaminotetraacetic acid, diethylenetriaminopentaacetic acid, and ethylenediaminodisuccinic acid, and their salts with water-soluble alkali metals. The bleach components can be added to the bar at a level up to 20%, preferably from about 1% to about 10%, more preferably from about 2% to about 6%.

Sodium sulfate is a well-known filler that is compatible with the compositions of this invention. It can be a by-product of the surfactant sulfation and sulfonation processes, or it can be added separately.

Calcium carbonate (also known as Calcarb) is also a well known and often used

component of laundry bars. Such materials are typically used at levels up to 40%, preferably from about 5% to about 25%.

Binding agents for holding the bar together in a cohesive, soluble form can also be used, and include natural and synthetic starches, gums, thickeners, and mixtures thereof.

Soil suspending agents can be used. In the present invention, their use is balanced with the fabric softening clay/clay flocculating agent combination to provide optimum cleaning and fabric softening performance. Soil suspending agents can also include water-soluble salts of carboxymethylcellulose and carboxyhydroxymethylcellulose. A preferred soil suspending agent is an acrylic/maleic copolymer, commercially available as Sokolan®, from BASF Corp. Other soil suspending agents include polyethylene glycols having a molecular weight of about 400 to 10,000, and ethoxylated mono- and polyamines, and quaternary salts thereof.

Optical brighteners are also preferred optional ingredients in laundry bars of the present invention. Preferred optical brighteners are diamino stilbene, distyrilbiphenyl-type optical brighteners. Preferred as examples of such brighteners are 4,4'-bis{[4-anilino-6-bis(2-hydoxyethyl) amino-1,3,5-trizin-2-yl]amino}stilbene-2,2'-disulfonic acid disodium salt, 4-4'-bis(2-sulfostyryl) biphenyl and 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl) amino]stilbene-2,2'-disulfonic acid disodium salt. Such optical brighteners, or mixtures thereof, can be used at levels in the bar of from about 0.05% - 1.0%.

Dyes, pigments, germicides, and perfumes can also be added to the bar composition.

Processing:

The detergent laundry bars of the present invention can be processed in conventional soap or detergent bar making equipment with some or all of the following key equipment: blender/mixer, mill or refining plodder, two-stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

In a typical process, the fabric softening clay and the clay flocculating are mixed, typically with other raw materials, in the blender. Alkylbenzene sulfonic acid (when used) is added into a mixture of alkaline inorganic salts (preferably which

includes sodium carbonate) and the resulting partially neutralized mixture is mechanically worked to effect homogeneity and complete neutralization of the mixture. Once the neutralization reaction is completed, the alkyl sulfate surfactant is added, followed by the remaining other ingredient materials. The mixing can take from 1 minute to 1 hour, with the usual mixing time being from 2 to 20 minutes. The blender mix is discharged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worn transfer conveyor.

The alkyl benzene sulfonic acid (HLAS) can be made by well-known processes, such as with SO_3 or oleum. It can be preferably to include excess inorganic sulfuric acid (H_2SO_4) in the stock of HLAS, which, upon neutralization, helps to increase the temperature of the product due to the heat of neutralization of the inorganic sulfuric acid.

Alternatively the fabric softening clay and the clay flocculating agent can, independently, be added at other times or places in the process, depending on the type of equipment and type of formulation to be made.

After milling or preliminary plodding, the product is then conveyed to a double stage vacuum plodder, operating at a high vacuum, e.g. 600 to 740 millimeters of mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

Examples of bars of the present invention are listed hereafter by way of exemplification, and not by way of limitation.

EXAMPLES

Various bar compositions can be made using the method described above.

	Example Number									
	1	2	3	4	5	6	7	8	9	10
	(weight percent)									
NaCFAS (C_{12-18})	19.13	16.88	25.50	22.50	22.50	13.50	13.50			25.50
Na(C_{12-18})LAS	3.38	5.63	4.50					20.00	25.00	4.50
Na_2CO_3	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
DTPP [1]	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	1.50
PEO-300M [2]	0.30	0.30	0.30	0.30				0.30		0.15
PEO-600M					0.20		0.20		0.20	
PEO-1.2MM						0.15				
Bentonite clay	10.0	10.0	10.0	10.0	12.0	12.0	12.0	10.0	12.0	10.0
Sokolan CP-5 [3]	0.70	0.70	0.70	0.70	0.70	0.70	1.00	0.70	0.70	0.70
TSPP			5.00							5.00
STPP	15.00	15.00	5.00	15.00	10.00	10.00		15.00	15.00	5.00
Zeolite	1.25	1.25	1.25	1.25	1.25	1.25	25.00	2.50	2.50	2.00
Sodium laurate						9.00	9.00			
SRP-A [4]	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.15
Protease enzyme [5]					0.10	0.10	0.10	0.10	0.10	
Amylase enzyme [6]					0.75	0.75		0.75	0.75	
Lipase enzyme					0.10			0.10		
Cellulase enzyme [7]					0.15	0.15	0.15		0.15	
	Balance [8]									

1. Sodium diethylenetriamine penta (phosphonate)
2. PEO is poly(ethylene oxide) having a molecular weight as indicated.
3. Sokolan CP-5 is maleic-acrylic copolymer
4. SRP-A is
$NaO_3S(CH_2CH_2O)_2$-C(O)-(C_6H_4)-C(O)O-[-CH_2CRH-O-C(O)-(C_6H_4)-C(O)O-]$_4$-
-[-CH_2CRH-O-C(O)-$(C_6H_4)SO_3$Na-C(O)O-]$_1$-$CH_2CH_2OCH_2CH_2SO_3Na$,

wherein R is H or CH_3 in a ratio of about 1.8:1.

5. Protease activity at 1 Au/gm stock.
6. Amylase activity at 100,000 amu/gm stock.

7. Carezyme® cellulase, supplied by Novo Nordisk, activity at 5000 Cevu/gm stock.

8. Balance comprises water (about 2% to 8%, including water of hydration), sodium sulfate, calcium carbonate, and other minor ingredients.

5

What is claimed is:

1. A laundry detergent bar comprising:
(a) detergent surfactant,
(b) detergency builder,
(c) fabric softening clay, and
(d) an amount of a clay flocculating agent to improve the clothes softening benefit of the fabric softening clay.

2. A laundry detergent bar according to claim 1 comprising:
(a) about 10% to about 60% by weight anionic surfactant,
(b) about 5% to about 60% by weight detergent builder,
(c) about 1% to about 30% of a smectite-type softening clay, and
(d) a polymeric clay flocculating agent at a level of about 0.001% to about 30% by weight of the fabric softening clay.

3. The laundry bar of Claim 2 wherein said anionic surfactant is selected from the group consisting of alkyl sulfate having an alkyl chain of from 10 to 20 carbon atoms, a linear-chain alkylbenzene sulfonate (LAS) having an alkyl chain of from 10 to 22 carbon atoms, a branched-chain alkylbenzene sulfonate (ABS) having an alkyl chain of from 10 to 22 carbon atoms, and mixtures thereof.

4. The laundry bar of Claim 3 wherein the surfactant comprises a mixture of alkyl sulfate (AS) and linear alkylbenzene sulfonate (LAS) in a molar ratio of AS:LAS from 70:30 to 100:0.

5. The laundry bar of Claim 2 wherein the detergent builder comprises sodium tripolyphosphate, tetrasodium pyrophosphate, or mixtures thereof.

6. The laundry bar of Claim 5 wherein the builder is from 10% to 20% sodium tripolyphosphate.

7. The laundry bar of Claim 2, comprising about 5% to about 20% of fabric softening clay.

8. The laundry bar of Claim 7, comprising about 8% to 14% of fabric softening

clay.

9. The laundry bar of Claim 8 wherein the fabric softening clay is bentonite.

10. The laundry bar of Claim 2 wherein the clay flocculating agent has a molecular weight of 100,000 to about 10 million.

11. The laundry bar of Claim 10 wherein the clay flocculating agent is poly(ethylene oxide).

12. The laundry bar of Claim 11 wherein the poly(ethylene oxide) polymer has a molecular weight of about 150,000 to about 5 million.

13. The laundry bar of Claim 12 wherein the poly(ethylene oxide) is comprised at a level of from about 0.5% to about 5%.

14. The laundry bar of Claim 2 further comprising about 0.1% to about 3% of a detergent chelant, selected from diethylenetriamine penta (methylene phosphonic acid), diethylenetriamine penta (acetic acid), alkali metal salts thereof, and mixtures thereof.

15. The laundry bar of Claim 14 wherein the detergent chelant is contained at a level of 0.2% to about 2%.

16. A laundry detergent bar comprising:
(a) about 18% to about 32% anionic surfactant, selected from alkyl sulfate, alkylbenzene sulfonate, and mixtures thereof,
(b) about 10% to about 20% phosphate builder selected from tripolyphosphate, pyrophosphate, and a mixture thereof,
(c) about 8% to about 14% of a smectite-type softening clay, and
(d) a polymeric poly(ethylene oxide) as a clay flocculating agent, at a level of about 0.5% to about 5% by weight of the fabric softening clay, and having a molecular weight between 150,000 and 3 million.

17. A laundry bar according to Claim 16, further comprising about 0.1% to about 3% of diethylenetriamine penta (methylene phosphonic acid), sodium salt.

INTERNATIONAL SEARCH REPORT

Interna[redacted]l Application No
[redacted]US 95/02947

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 707 289 (P.N.RAMACHANDRAN ET AL.) 17 November 1987 see column 5, line 52 see claims ---	1
Y	EP,A,0 299 575 (PROCTER & GAMBLE CO.) 18 January 1989 cited in the application see the whole document ---	1
P,A	GB,A,2 276 630 (UNILEVER PLC) 5 October 1994 see page 8, line 8 - line 9 see page 9, line 24 see claims --- -/--	1-17

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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Date of the actual completion of the international search	Date of mailing of the international search report
20 June 1995	[illegible] 07.95

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 127 426 (UNILEVER PLC) 11 April 1984 see the whole document	1-17
P,A	WO,A,94 23010 (UNILEVER NV ET AL.) 13 October 1994	1
A	GB,A,2 145 109 (COLGATE PALMOLIVE CO) 20 March 1985 see the whole document & US,A,4 543 204 cited in the application	1-17

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INTERNATIONAL SEARCH REPORT

Inter[redacted]l Application No
P[redacted]S 95/02947

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4707289	17-11-87	NONE		
EP-A-0299575	18-01-89	DE-D-	3887020	24-02-94
		DE-T-	3887020	09-06-94
		JP-A-	1098697	17-04-89
GB-A-2276630	05-10-94	NONE		
GB-A-2127426	11-04-84	NONE		
WO-A-9423010	13-10-94	AU-B-	6426794	24-10-94
GB-A-2145109	20-03-85	US-A-	4543204	24-09-85
US-A-4543204	24-09-85	GB-A-	2145109	20-03-85